

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
7 December 2000 (07.12.2000)

PCT

(10) International Publication Number  
**WO 00/72817 A1**

- (51) International Patent Classification<sup>7</sup>: A61K 7/48, C08L 83/04, C08J 3/09
- (21) International Application Number: PCT/US00/13810
- (22) International Filing Date: 19 May 2000 (19.05.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
09/322,526 28 May 1999 (28.05.1999) US
- (71) Applicant: NEUTROGENA CORPORATION  
[US/US]; 5760 West 96th Street, Los Angeles, CA 90045 (US).
- (72) Inventors: STAHL, Chris, R.; 743 W. 36th Street, San Pedro, CA 90731 (US). WOODIN, Frederick, W., Jr.; 227 S. Irena Avenue #10, Redondo Beach, CA 90277 (US). KUNG, John; 58 Lyle Place, Edison, NJ 08820 (US). LIU, Jue-Chen; 268 Berkley Avenue, Belle Mead, NJ 08502 (US).
- (74) Agents: CIAMPORCERO, Audley, A. et al.; One Johnson and Johnson Plaza, New Brunswick, NJ 08933 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— With international search report.  
— Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 00/72817 A1

(54) Title: WATER-IN-OIL EMULSION COMPRISING A SILICONE GEL CONTAINING VITAMIN C

(57) Abstract: The present invention relates to a water-in-oil emulsion containing a silicone gel that comprises a volatile liquid, a silicone polymer, and ascorbic acid, and methods of using such emulsion for treating skin disorders.

WATER-IN-OIL EMULSION COMPRISING A SILICONE GEL  
CONTAINING VITAMIN C

BACKGROUND OF THE INVENTION

Ascorbic acid (Vitamin C) is well known for its collagen stimulation, free radical scavenging, and tyrosinase inhibiting activities in the skin. Because of its powerful anti-oxidant properties, ascorbic acid is very sensitive to oxygen and, thus, difficult to stabilize. The degradation of ascorbic acid in the product is observable to consumers by the yellowing or browning of the product and/or the existence of a malodor. Since ascorbic acid rapidly degrades in these formulations, the consumer, thus, is not receiving all, if any, of the therapeutic benefit of the vitamin.

In addition, since ascorbic acid destabilizes in the presence of water, its inclusion in an emulsion system often compromises the aesthetics of the emulsion due to the formation of a brown color. Its inclusion in an anhydrous composition is also undesirable because of the composition's greasy and heavy texture.

Because of these stability problems, many cosmetic products have utilized derivatives of ascorbic acid that have improved stability. These derivatives, however, need to be subsequently metabolized into ascorbic acid to have a therapeutic effect. This metabolism often does not happen to any significant effect in the skin.

The present invention relates topical water-in-oil emulsion (e.g., where the continuous oil phase contains the oil soluble agents and the discontinuous water phase

contains the water soluble agents) comprising a silicone gel containing ascorbic acid. The silicone gel protects the ascorbic acid from degradation, thereby, providing the consumer the benefit of the vitamin. Also, as the ascorbic acid is protected within the silicone gel, the emulsion of the present invention can have a significant (e.g., over 50%, by weight) water content.

#### SUMMARY OF THE INVENTION

In one aspect, the invention features a water-in-silicone emulsion comprising a silicone gel, wherein the silicone gel comprises a volatile liquid, a silicone polymer, and ascorbic acid. In one embodiment, the silicone polymer is polysilicone-11. In one embodiment, the volatile liquid is a silicone fluid (e.g., cyclomethicone). In one embodiment, the silicone gel further comprises petrolatum and/or a second liquid (e.g., a silicone liquid such as dimethicone). In one embodiment, the silicone gel further comprises a porous silica (e.g., having a pore volume of 0.1 to about 1 ml/g, a particle diameter of between 1 - 20 microns, and/or an oil absorbence of between 10-500 ml/100g).

In one embodiment, the silicone gel comprises by weight: (a) about 0.01% to about 99% (e.g., about 10% and 90%) of the volatile liquid (e.g., cyclomethicone); (b) about 0.01% to about 90% (e.g., about 30% to about 70%) of the silicone polymer (e.g., polysilicone-11); and (c) about 0.001% to about 50% (e.g., about 1% and about 20%) of the ascorbic acid. In a further embodiment, the silicone gel further comprises by weight: (d) about

0.001% to about 60% (e.g., about 0.001% to about 30%) of petrolatum and/or (e) about 0.001% to about 50% (e.g., about 0.001% to about 30%) of porous silica. In one embodiment, the emulsion (e.g., within the water phase, oil phase, or the silicone gel) further comprises a dermatologically active agent such as a retinoid (e.g., retinol, retinal, retinoic acid, retinyl acetate, and retinyl palmitate) or an  $\alpha$ -hydroxy acid, a  $\beta$ -hydroxy acid, or poly-hydroxy acid such as glycolic acid, salicylic acid, lactic acid, citric acid, malic acid, and azaleic acid.

In one embodiment, the water-in-oil emulsion comprises by weight: (a) about 0.001% to about 50% (e.g., about 5% to about 50%) of the silicone gel; (b) about 0.001% to about 90% (e.g., about 5% to about 50%) of water; and (c) about 0.001% to about 50% of an oil such as a hydrocarbon or silicone liquid. In one embodiment, the hydrocarbon is a member selected from the group consisting of branched or straight chained C8-C40 (e.g., C12-20) hydrocarbons (e.g., isododecane, isoparaffins, isoeicosane, and isohexadecane) and said silicone liquid is selected from the group consisting of cyclomethicone and dimethicone, or mixtures thereof.

In a further embodiment, the composition further comprises a sunscreen, e.g., about 0.001% to about 50% (e.g., about 0.001 to about 20%) of sunscreen (e.g., titanium dioxide, phenylbenzimidazole sulfonic acid, octyl methoxycinnamate, avobenzone, or mixtures thereof). In a further embodiment, the oil-phase and/or the water

phase of the emulsion comprise an antioxidant (e.g., N-acetyl-L-cysteine).

In another aspect, the present invention features method of preventing or treating skin disorders (e.g., protecting skin from photo-damage, preventing collagen breakdown, eliminating free radicals, stimulating collagen synthesis, reducing skin discoloration, evening skin tones, firming the skin, and reducing the signs of skin aging), the method comprising applying to the skin (e.g., the hands or face) of a subject an effective amount of the above mentioned emulsion. In one embodiment, the emulsion is applied to the skin one to three times daily.

Other features and advantages of the present invention will be apparent from the detailed description of the invention and from the claims.

#### DETAILED DESCRIPTION OF THE INVENTION

It is believed that one skilled in the art can, based upon the description herein, utilize the present invention to its fullest extent. The following specific embodiments are to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention belongs. Also, all publications, patent applications, patents, and other references mentioned herein are incorporated by reference.

The present invention relates to a novel water-in-oil emulsion comprising a silicone gel that both stabilizes and delivers ascorbic acid. The gel also possessing oil-absorbing (e.g., sebum absorbing) properties. The silicone gel is made, in one embodiment, by dispersing oil swellable silicone polymer (e.g., polysilicone-11) in a volatile liquid (e.g., silicone fluid such as cyclomethicone) or a volatile liquid mixed with other ingredients (e.g., dimethicone and/or petrolatum). Ascorbic acid is then dispersed in the silicone gel, e.g., by either (i) adding ascorbic acid powder to the silicone gel and milling the mixture to ensure homogeneous distribution of the ascorbic acid in the gel or (ii) dissolving the ascorbic acid in a solvent (e.g., a polar solvent such as polyethylene glycols) and then uniformly dispersing the ascorbic acid solution in the silicone gel. Ascorbic acid is available from a number of commercial sources such as Roche in Parsippany, New Jersey. A silicone gel containing ascorbic acid (i.e., Gransil PSAA) is also available from Grant Industries in Elmwood Park, NJ.

Upon spreading on skin (e.g., the hands or facial skin), the silicone gel releases the volatile liquid, delivers ascorbic acid to the skin, and absorbs non-volatile excess skin oil present on the skin (e.g., the oil is absorbed by the oil-swellable silicone polymer and, if present, porous silica). The composition's ability to absorb sebum helps the skin maintain an environment that is less conducive to clogged pores, thereby, inhibiting the formation of comedones. The

silicone gel may also contain porous silica that further enhances the oil-absorbing properties of the gel. The gel additionally has the ability to scatter incoming rays of light in all directions. By diminishing reflected light, the skin, thus, has a smooth matte appearance.

As used herein, the term "volatile" refers to those liquids that have a measurable vapor pressure at ambient temperature. Examples of volatile liquids include branched or straight chained hydrocarbons (e.g., C3-C20 hydrocarbons such as isoparaffins, isoeicosane, isohexadecane and isododecane) and silicone fluids. Examples of volatile silicone fluids include the following: cyclic and linear polydimethylsiloxanes containing from about 3 to about 9 (e.g., from about 4 to about 5) silicone atoms such as cyclomethicones; Dow Corning 200, Dow Corning 344, and Dow Corning 345 (manufactured by Dow Corning, Midland, MI); Silicone 7158 and 7207 (manufactured by Union Carbide, Houston, TX); SF 1202 (manufactured by General Electric); and SWS-03314 (manufactured by SWS Silicones, Inc.). As used herein, the term cyclomethicone refers to cyclotrisiloxane, cyclotetrasiloxane, cyclopentasiloxane, cyclohexasilxane, or mixtures thereof.

The silicone polymers of the present invention may have an average molecular weight in excess of 10,000 (e.g., between about 10,000 and 10,000,000). Examples of silicone polymers include crosslinked siloxane (e.g., dimethicone or a dimethicone derivative) copolymers such as stearyl methyl-dimethyl siloxane copolymer (Gransil SR-CYC, available from Grant Industries); Polysilicone-11

(i.e., a crosslinked silicone rubber formed by the reaction of vinyl terminated silicone and methylhydrodimethyl siloxane in the presence of cyclomethicone), cetearyl dimethicone/vinyl dimethicone crosspolymer (i.e., a copolymer of cetearyl dimethicone crosslinked with vinyl dimethyl polysiloxane), dimethicone/phenyl vinyl dimethicone crosspolymer (i.e., copolymer of dimethylpolysiloxane crosslinked with phenyl vinyl dimethylsiloxane), and dimethicone/vinyl dimethicone crosspolymer (i.e., copolymer of dimethylpolysiloxane crosslinked with vinyl dimethylsiloxane).

The silicone gels may also be purchased from commercial suppliers such as Grant Industries. Examples of such gels include cyclomethicone (and) polysilicone-11 (Gransil GCM5), cyclotetrasiloxane(D4) (and) petrolatum (and) polysilicone-11 (Gransil PS-4), cyclopentasiloxane(D5) (and) petrolatum (and) polysilicone-11 (Gransil PS-5), cyclopentasiloxane(D5) (and) dimethicone (and) polysilicone-11 (Gransil DMCM-5), cyclotetrasiloxane(D4) (and) dimethicone (and) polysilicone-11(Gransil DMCM-4), polysilicone-11 (and) isododecane (Gransil IDS), and cyclomethicone (and) polysilicone-11 (and) petrolatum (and) phytosphingosine (Gransil SPH). Examples of such gels available from General Electric include cyclopentasiloxane (and) dimethicone/vinyl dimethicone crosspolymer (SFE839).

The water-in-oil emulsion may also contain other cosmetically acceptable agents that are numerous and varied, but are also well known to one skilled in the



art. In one aspect, the emulsion (i.e., the composition) comprises one or more of the members selected from the group consisting of acidifying agents, alkalizing agents, aerosol propellants, antimicrobial agents, antioxidants, buffering agents, chelating agents, coloring additives, dermatologically active agents, dispersing agents, emollients, emulsifying agents, humectants, fragrances, masking agents, preservatives, sugars, sunscreen agents, surfactants, suspending agents, and thickening agents.

These ingredients are discussed below. Examples of these agents are listed below as well as in the International Cosmetic Ingredient Dictionary and Handbook, eds. Wenninger and McEwen (The Cosmetic, Toiletry, and Fragrance Assoc., Washington, D.C., 7<sup>th</sup> Edition, 1997) (hereinafter "ICT Handbook").

Acidifying and alkalizing agents are added to obtain the desired pH of the water phases of the composition. Examples of acidifying agents included acetic acid, citric acid, glacial acetic acid, malic acid, and proprionic acid. Examples of alkalizing agent include edetol, potassium carbonate, potassium hydroxide, sodium borate, sodium carbonate, and sodium hydroxide. Other acidifying or alkalizing agents are listed on page 1653 of the ICT Handbook.

Aerosol propellants are used when the composition is to be administered as an aerosol under pressure. Examples of aerosol propellants include halogenated hydrocarbons such as dichlorodifluoromethane, dichlorotetrafluoroethane, and trichloromonofluoromethane, nitrogen, and volatile

hydrocarbons such as butane, propane, isobutane, or mixtures thereof. Other propellants are listed on page 1655 of the ICT Handbook.

5 Anti-microbial agents are used when the area that the composition is to be applied is prone to microbial infection, e.g., by bacteria, fungal, or protozoa. Examples of such agents include benzyl alcohol, chlorobutanol, phenylethyl alcohol, phenylmercuric acetate, potassium sorbate, and sorbic acid, benzoic  
10 acid, butyl paraben, ethyl paraben, methyl paraben, propyl paraben, and sodium benzoate. Other anti-microbial agents are listed on page 1612 of the ICT Handbook.

Antioxidants are used to protect ingredients (e.g.,  
15 ascorbic acid in the silicone gel) of the composition from oxidizing agents that are included within or come in contact with the composition. Examples of antioxidants include water soluble antioxidants such as grape seed extract, camellia oleifera extract, N-acetyl-  
20 L-cysteine, ascorbic acid, sodium sulfite, sodium formaldehyde, isoascorbic acid, cysteine hydrochloride, 1,4-diazobicyclo-(2,2,2)-octane, and mixtures thereof. Examples of oil-soluble antioxidants include ascorbyl palmitate, butylated hydroxyanisole, butylated  
25 hydroxytoluene, potassium propyl gallate, octyl gallate, dodecyl gallate, phenyl- $\alpha$ -naphthyl-amine, and tocopherols such as  $\alpha$ -tocopherol. Other antioxidants are listed on pages 1612-13 of the ICT Handbook.

30 Buffering agents are used to maintain an established pH of the water phase of the composition.

Examples of buffering agents included triethanolamine sodium citrate, calcium acetate, potassium metaphosphate, potassium phosphate monobasic, and tartaric acid. Other buffering agents are listed on page 1653 of the ICT Handbook.

Chelating agents are used to maintain the ionic strength of the composition and/or bind to destructive compounds and metals that are included within or come in contact with the composition. Examples of chelating agents included dihydroxy ethyl glycine, citric acid, tartaric acid, edatate dipotassium, edetate disodium, edetic acid, and ethylenediamine tetracetic acid (EDTA) and its salts (e.g., tetrasodium EDTA). Other chelating agents are listed on page 1626 of the ICT Handbook.

Coloring additives are used to add color to the composition. Examples of such coloring additives include titanium dioxide, FDC colors such as Yellow #5, yellow iron oxide, red iron oxide, black iron oxide, caramel, carmine, fluorescein derivatives, methoxsalen, trioxsalen, carbon black, azo dyes, anthraquinone dyes, blue azulenes, guajazulene, chamuzulene, erythrosin, bengal rose, phloxin, cyanosin, daphnin, eosin G, cosin 10B, and Acid Red 51. Other coloring agents are listed on pages 1628-30 of the ICT Handbook.

Dermatologically active agents include agents for treating wound healing, inflammation, acne, psoriasis, cutaneous aging, skin cancer, impetigo, herpes, chickenpox, dermatitis, pain, itching, and skin irritation. Examples of such dermatologically active agents include hydrocortisone, dexamethesone, panthenol,

phenol, tetracycline hydrochloride, yeast,  
hexylresorcinol, lamin, kinetin, betamethasone,  
triamcinolone, fluocinolone, methylprednisolone,  
retinoids such as retinol and retinoic acid, dapsone,  
5 sulfasalazine, resorcinol, salicylic acid, benzoyl  
peroxide, erythromycin-benzoyl peroxide, erythromycin,  
clindamycin, mupirocin, griseofulvin, azoles such as  
miconazole, econazole, itraconazole, fluconazole, and  
ketoconazole, ciclopirox, allylamines such as naftifine  
10 and terfenadine, acyclovir, famciclovir, valacyclovir,  
benzocaine, lidocaine, dibucaine, pramoxine  
hydrochloride, methyl salicylate, camphor, menthol,  
resorcinol, and vitamins such as tocopherol, tocopheryl  
acetate, pantothenic acid, panthenol, ascorbic acid,  
15 biotin, and retinoids such as retinol, retinoic acid,  
retinal, retinyl acetate, and retinyl palmitate,  $\alpha$ -  
hydroxy acid, a  $\beta$ -hydroxy acid, or poly-hydroxy acid  
such as glycolic acid, lactic acid, citric acid, malic  
acid, and azaleic acid, and sunless tanning agents such  
20 as 1,3-dihydroxyacetone and 1,3,4-trihydroxy-2-butanone  
(erythulose).

Examples of dispersing and suspending agents  
include quarternium-18 hectorite, polyhydroxy stearic  
acid, poligeenan and silicon dioxide. Other dispersing  
25 and suspending agents are listed on page 1690-91  
of the ICT Handbook.

Emollients are agents that soften and smooth the  
skin. Examples of emollients include hydrocarbon oils  
and waxes (e.g., natural and synthetic waxes) such as  
30 mineral oil, petrolatum, microcrystalline wax,

polyethylene, triglyceride esters such as those of  
castor oil, cocoa butter, safflower oil, cottonseed oil,  
corn oil, olive oil, cod liver oil, almond oil, avocado  
oil, palm oil, sesame oil, squalene, and soybean oil,  
5 acetylated monoglycerides, ethoxylated glycerides, fatty  
acids, alkyl esters of fatty acids, alkenyl esters of  
fatty acids, fatty alcohols, fatty alcohol ethers,  
ether-esters, lanolin and derivatives of lanolin,  
polyhydric alcohol esters, wax esters such as beeswax,  
10 vegetable waxes, phospholids, and sterols. Other  
emollients are listed on pages 1656-61 of the ICT  
Handbook.

Emulsifying agents are used for preparing emulsions  
of the present invention. Examples of emulsifying  
15 agents used for preparing water-in-oil emulsions include  
cyclomethicone (and) dimethicone copolyol, cetyl  
dimethicone copolyol, polyglyceryl-4 isostearate, hexyl  
laurate, PEG-30 dipolyhydroxystearate, and PEG-40  
sorbitan peroleate. Other emulsion are listed on pages  
20 1679-87 of the ICT Handbook. Emulsion stabilizers are  
listed on pages 1634-35 of the ICT Handbook.

Humectants are agents that promote the retention of  
moisture, e.g., moisturizers. Examples of humectants  
include sorbitol, matricaria extract, aloe barbadensis  
25 gel, glycerin, glycereth 5 lactate, glycereth 7  
triacetate, glycereth 7 diisononoate, hexanetriol,  
hexylene glycol, propylene glycol, dipropylene glycol,  
alkoxylated glucose, D-panthenol, 1-2-pantandiol, 2-  
methyl-1,3-propanediol, and derivatives thereof, and

hyaluronic acid. Other humectants are listed on pages 1661-62 of the ICT Handbook.

5        Examples of fragrances include peppermint, rose oil, rose water, aloe vera, clove oil, menthol, camphor, eucalyptus oil, and other plant extracts. Certain fragrances may require a solubilizer, e.g., PPG-5-ceteareth-20. To eliminate certain odors from compositions, masking agents may be used. An example of a masking agent includes ethylene brassylate. Other  
10       fragrances and masking agents are listed on pages 1639-40 of the ICT Handbook.

      Preservatives are used to protect the composition from degradation. Examples of preservatives include liquipar oil, phenoxyethanol, methyl paraben, propyl  
15       paraben, butyl paraben, isopropyl paraben, isobutyl paraben, diazolidinyl urea, imidazolidinyl urea, diazolidinyl urea, benzalkonium chloride, benzethonium chloride, phenol, and mixtures thereof (e.g., the paraben mixture Liquipar Oil). Other preservatives are  
20       listed on pages 1654-55 of the ICT Handbook.

      Examples of sugars include monosaccharides, disaccharides, and polysaccharides such as glucose, xylose, fructose, reose, ribose, pentose, arabinose, allose, tallose, altrose, mannose, galactose, lactose,  
25       sucrose, erythrose, glyceraldehyde, or any combination thereof.

      Sunscreen agents are agents used to block or reduce the amount of ultraviolet radiation impinging on the skin (e.g., by absorption, scattering, and reflection of  
30       the ultraviolet radiation). Segarin, et al., Cosmetics

Science and Technology, Chapter VIII, pages 189, et seq. discloses numerous examples of sunscreen agents.

5        Examples of sunscreen agents include both organic compounds and their salts such as phenylbenzimidazole sulfonic acid, octyl methoxycinnamate, octyl salicylate, benzophenone-3 homosalate, octocrylene, avobenzene, and menthyl anthranilate, as well as inorganic particulate materials such as zinc oxide and titanium dioxide. Other  
10        sunscreen agents are listed on page 1672 of the ICT Handbook. Generally, the composition will contain from about 1% to about 50%, by weight, of sunscreen agent(s). The exact amounts will vary depending on the sunscreen used and the desired sun-protection factor (SPF), e.g., and SPF of at least 15 or an SPF of at least 30.

15        Surfactants are agents used to stabilize multi-component compositions, e.g., used as wetting agents, antifoam agents, emulsifiers, dispersing agents, and penetrants. Examples of surfactants include methyl gluceth 20, decyl polyglucoside, lauryl chloride,  
20        laureth 4, laureth 9, monoethanolamine, nonoxynol 4, nonoxynol 9, nonoxynol 10, nonoxynol 15, nonoxynol 30, poloxalene, polyoxyl 8, 40, and 50 stearate, polysorbate 20, polysorbate 40, polysorbate 60, polysorbate 65, polysorbate 80, and polysorbate 85, sodium lauryl  
25        sulfate, sorbitan and its derivatives. Other surfactants are listed on page 1672-90 of the ICT Handbook.

30        The emulsion that may be in a number of different delivery forms, e.g., a spray, mist, aerosol, shampoo, hair conditioner, mousse, semi-solid cream, liquid

lotion, gel, or other suitable forms intended to be applied to the skin of a subject (e.g., a human). Water-in-oil emulsions (e.g., ratio of about 8:1 to about 1:100 such as about 3:1 to about 1:10 of water to oil) are typically used in preparing lotions and creams of the present invention. The actual ratio of the two phases will depend on the consistency of the desired final product. The viscosity of the compositions of the present invention may be different dependent upon the type of formulation being prepared, e.g., a liquid formulation will have a lower viscosity than a cream formulation. Typically, the viscosity of liquid formulations of the present invention will range from 5,000 to 25,000 cps. Bulking agents may be used to increase the viscosity of the composition. Examples of bulking/thickening agents are talc, quaternium-18 hectorite, and paraffin wax. Other bulking agents are listed on page 1625-26 of the ICT Handbook. Other viscosity increasing agents are listed on pages 1693-97 of the ICT Handbook. Viscosity decreasing agents are listed on pages 1692-92 of the ICT Handbook.

The emulsion of the present invention may be prepared using methodology that is well known by an artisan of ordinary skill (e.g., by using well-known mixing and blending procedures). For examples, for emulsion compositions of the present invention, each phase of the emulsion may be separately prepared with all of the components contained in their appropriate phases. The emulsion is then formed by adding one phase to the other phase with agitation.



The emulsion of the present invention may be packaged in a container that is well known by an artisan of ordinary skill. The emulsion is preferably packaged in a container that minimizes exposure to oxygen (e.g., aluminum or laminate tubes). The tubes may be purged with an inert gas, such as nitrogen or argon, before sealing.

The following is a description of the manufacture of five compositions of the present invention. Other compositions of the invention can be prepared in an analogous manner by a person of ordinary skill in the art.

Example 1: Water-in-oil Emulsion Skin Cream

The ingredients and their respective weight percentages with respect to the total composition for Composition 1 are recited below in Table 1.

Table 1

INGREDIENT	WEIGHT (%)
Phase A ("Oil Phase")	
Isohexadecane	8
Cyclomethicone (and) Petrolatum (and) ascorbic Acid ( and) Polysilicone-11	10
Quaternium-18 Hectorite	1
Cyclomethicone	2
Propylparaben	0.1
BHT	0.1
Tocopheryl Acetate	0.5
Cetyl Dimethicone Copolyol (and) polyglyceryl-4 isostearate (and) hexyl laurate (30:40:30)	5
Methyl paraben	0.3
Octyl methoxycinnamate	5.5
Paraffin wax	1

<b>Phase B ("Water Phase")</b>	
Water	62.5
Triethanolamine	0.55
Phenylbenzimidazole sulfonic acid	1
Phenoxyethanol	1
Sodium chloride	0.6
Panthenol	0.5
Disodium EDTA	0.1
Butylene Glycol (and) water (and) camellia oleifera extract (40:40:20)	0.2
<b>Phase C</b>	
Tocopherol	<u>0.05</u>
	100.00

The suppliers of the following ingredients are indicated: Quaternium-18 hectorite (Bentone 38CG; Rheox, Hightstown, NJ); Cetyl Dimethicone Copolyol (and) polyglyceryl-4 isostearate (and) hexyl laurate (Abil WE-09); Goldschmidt, Hopewell, NJ); Butylene Glycol (and) water (and) camellia oleifera extract (Actiquench GTB-20; Active Organics, Dallas, TX); and Cyclomethicone (and) Petrolatum (and) Polysilicone-11 (and) Ascorbic Acid (weight percentages between the ingredients as follows- (70:15:10:5)- Gransil PSAA or (65:15:15:5)- Gransil PSAA15-05 MV), Grant Industries, Elmwood Park, NJ). . The cyclomethicone used the silicone gel was cyclotetrasiloxane, but other cyclomethicones may be used (e.g., cyclopentasiloxane).

First, quaternium-18 hectorite was homogeneously dispersed in the isohexadecane in the main closed kettle. A Krieger or Fryma type kettle may be used in order to draw a vacuum during processing to protect the ascorbic acid from oxidation. The remainder of the Phase A ingredients were then added to the main kettle. The

resulting mixture was heated to 65°C until the paraffin wax melted. The mixture was then cooled to 45°C ("Phase A Mixture").

The Phase B ingredients were combined in a second kettle, mixed until homogenous, and heated to 45°C ("Phase B Mixture"). The Phase B Mixture was then added to the main kettle containing the Phase A Mixture and allowed to mix until the emulsion formed. The resulting mixture was then homogenized with a Gifford-Wood homogenizer (Model 1L, Hudson, NH) until a glossy white cream formed ("Phase AB Mixture").

The Phase AB Mixture was cooled to 50°C, and tocopherol was then added to the mixture. The resulting Composition 1 had a 1% ascorbic acid activity, a viscosity of 55,000 cps, and a sunscreen activity estimated at SPF 15.

#### Example 2: Water-in-oil Emulsion Skin Cream

The ingredients and their respective weight percentages with respect to the total composition for Composition 2 are recited below in Table 2.

Table 2

INGREDIENT	WEIGHT (%)
Phase A ("Oil Phase")	
Isododecane	8

Cyclomethicone (and) Petrolatum (and) ascorbic Acid (and) Polysilicone-11 (70:15:10:5)	10
Quaternium-18 Hectorite	1
Cyclomethicone	2
Propylparaben	0.1
BHT	0.1
Tocopheryl Acetate	0.5
Ceryl Dimethicone Copolyol (and) polyglyceryl-4 isostearate (and) hexyl laurate (30:40:30)	5
Methyl paraben	0.3
Ascorbyl Palmitate	0.02
Octyl methoxycinnamate	5.5
Paraffin wax	1
<b>Phase B ("Water Phase")</b>	
Water	61.92
Triethanolamine	0.55
Phenylbenzimidazole sulfonic acid	1
Phenoxyethanol	1
Sodium chloride	0.6
Panthenol	0.5
Yellow #5, 1% solution	0.3
Butylene Glycol (and) water (and) grape seed extract	0.2
Butylene Glycol (and) water (and) camellia oleifera extract (40:40:20)	0.2
N-acetyl-L-cysteine	0.01
<b>Phase C</b>	
Tocopherol	0.2
	100.00

The suppliers of the following ingredients are indicated: Butylene Glycol (and) water (and) grape seed extract (Actiphyte Grape Seed BG50P; Active Organics, Dallas, TX); and N-acetyl-L-cysteine (Tanabe USA, San Diego, CA).

This Composition 2 was manufactured according to the procedure set forth in Example 1. This composition contains various antioxidants in both the water and oil phases. It also contains an artificial yellow color. No

discoloration of the cream was observable following one month of accelerated stability at either 40°C or 50°C. Composition 2 also had a 1% ascorbic acid activity, a viscosity of 20,000 cps, and a sunscreen activity estimated at SPF 15.

### Example 3: Water-in-oil Emulsion Skin Cream

The ingredients and their respective weight percentages with respect to the total composition for Composition 3 are recited below in Table 3.

Table 3

INGREDIENT	WEIGHT (%)
<b>Phase A ("Oil Phase")</b>	
Isohexadecane	6
Cyclomethicone (and) Petrolatum (and) ascorbic Acid ( and) Polysilicone-11 (70:15:10:5)	20
Quaternium-18 Hectorite	1
Propylparaben	0.1
BHT	0.1
Tocopheryl Acetate	0.5
Cetyl Dimethicone Copolyol (and) polyglyceryl-4 isostearate (and) hexyl laurate (30:40:30)	5
Methyl paraben	0.3
Octyl methoxycinnamate	5.5
Paraffin wax	1
<b>Phase B ("Water Phase")</b>	
Water	56.5
Triethanolamine	0.55
Phenylbenzimidazole sulfonic acid	1
Phenoxyethanol	1
Sodium chloride	0.6
Panthenol	0.5
Disodium EDTA	0.1
Butylene Glycol (and) water (and) camellia oleifera extract (40:40:20)	0.2

<b>Phase C</b>	
Tocopherol	0.05
	100.00

This Composition 3 was manufactured according to the procedure set forth in Example 1. The resulting Composition 1 had a higher level of ascorbic acid activity (i.e., 2%), a viscosity of 190,000 cps, and a sunscreen activity estimated at an SPF 15.

Example 4: Water-in-oil Emulsion Skin Cream

The ingredients and their respective weight percentages with respect to the total composition for Composition 4 are recited below in Table 4.

Table 4

INGREDIENT	WEIGHT (%)
<b>Phase A ("Oil Phase")</b>	
Isododecane	6
C12-15 Alkyl Benzoate	6
Cyclomethicone (and) Petrolatum (and) ascorbic Acid ( and) Polysilicone-11 (70:15:10:5)	10
Quaternium-18 Hectorite	1
Cyclomethicone	2
Propylparaben	0.1
BHT	0.1
Tocopheryl Acetate	0.5
Cetyl Dimethicone Copolyol (and) polyglyceryl-4 isostearate (and) hexyl laurate (30:40:30)	5
Methyl paraben	0.3
Ascorbyl Palmitate	0.02
Octyl methoxycinnamate	5.5
Avobenzone	3
Paraffin wax	1

<b>Phase B ("Water Phase")</b>	
Water	56.77
Phenoxyethanol	1
Sodium chloride	0.6
Panthenol	0.5
Yellow #5, 1% solution	0.3
Camellia Oleifera Extract	0.1
N-acetyl-L-cysteine	0.01
<b>Phase C</b>	
Tocopherol	0.2
	100.00

Camellia Oleifera Extract was purchased as Green Tea Extract from Dragoco, Totowa, NJ.

This Composition 4 was manufactured according to the procedure set forth in Example 1, but isododecane was used in place of isohexadecane. This composition contains avobenzone (Parsol 1789, Roche, Parsippany, NJ) for additional UVA protection. The addition of C12-15 alkyl benzoate assists in the solubility of the avobenzone. The resulting Composition 4 had a 1% ascorbic acid activity, a viscosity of 14,000, and a sunscreen activity estimated SPF 15.

#### Example 5: Water-in-oil Emulsion Skin Cream

The ingredients and their respective weight percentages with respect to the total composition for Composition 5 are recited below in Table 5.

Table 5

<u>INGREDIENT</u>	<u>WEIGHT (%)</u>
<b>Phase A ("Oil Phase")</b>	
Isododecane	8

Cyclomethicone (and) Petrolatum (and) ascorbic Acid ( and) Polysilicone-11 (70:15:10:5)	10
Quaternium-18 Hectorite	1
Cyclomethicone	2
Propylparaben	0.1
BHT	0.1
Tocopheryl Acetate	0.5
Cetyl Dimethicone Copolyol (and) polyglyceryl-4 isostearate (and) hexyl laurate (30:40:30)	5
Methyl paraben	0.3
Ascorbyl Palmitate	0.02
Octyl methoxycinnamate	5.5
Paraffin wax	1
<b>Phase B ("Water Phase")</b>	
Water	62.14
Triethanolamine	0.55
Phenylbenzimidazole sulfonic acid	1
Phenoxyethanol	1
Sodium chloride	0.6
Panthenol	0.5
Yellow #5, 1% solution	0.2
Camellia Oleifera Extract	0.1
N-acetyl-L-cysteine	0.01
Retinol (and) polysorbate 20 (50:50)	0.18
<b>Phase C</b>	
Tocopherol	0.05
	100.00

The retinol (and) polysorbate 20 was purchased from BASF in Mt. Olive, NJ.

This Composition 5 was manufactured according to the procedure set forth in Example 1, but isododecane was used instead of isohexadecane. The resulting Composition 5 contained retinol for enhanced skin conditioning properties. The Composition also had 1 % ascorbic acid activity, a viscosity of 31,000, and a sunscreen activity estimated at SPF 15.



It is understood that while the invention has been described in conjunction with the detailed description thereof, that the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the claims.

What is claimed is:

Claims

1. A water-in-silicone emulsion comprising (i) a  
silicone gel, wherein said gel comprises a volatile  
liquid, a silicone polymer, and ascorbic acid, and (ii)  
about 30% to about 70% by weight, of water.

2. An emulsion of claim 1, wherein said silicone  
gel further comprises petrolatum.

3. An emulsion of claim 2, wherein said silicone  
polymer is polysilicone-11.

4. An emulsion of claim 2, wherein said volatile  
liquid is a silicone.

5. An emulsion of claim 4, wherein said volatile  
liquid is cyclomethicone.

6. An emulsion of claim 3, wherein said volatile  
liquid is cyclomethicone.

7. An emulsion of claim 1, wherein said silicone  
gel comprises by weight:

(a) about 0.01% to about 99% of a volatile liquid;

(b) about 0.01% to about 90% of a silicone polymer;

and

(c) about 0.001% to about 30% of ascorbic acid.

8. An emulsion of claim 1, wherein said silicone gel comprises by weight:

- (a) about 0.01% to about 99% of cyclomethicone;
- (b) about 0.01% to about 90% of polysilicone-11; and
- (c) about 0.001% to about 30% of ascorbic acid.

9. An emulsion of claim 8, wherein said silicone gel further comprises by weight:

- (d) about 0.001% to about 60% of petrolatum.

10. An emulsion of claim 1, wherein said emulsion further comprises a retinoid.

11. An emulsion of claim 1, wherein said silicone gel further comprises a retinoid.

12. An emulsion of claim 1, wherein said emulsion comprises by weight:

- (a) about 0.01% to about 50% of said silicone gel;
- and
- (b) about 0.01% to about 50% of an oil.

13. An emulsion of claim 1, wherein said composition comprises about 50% to about 70%, by weight, of water.

14. An emulsion of claim 13, wherein said oil is a member selected from the group consisting of branched and straight chained C8-C40 hydrocarbons and silicone liquids.

15. An emulsion of claim 14, wherein said composition comprises a hydrocarbon selected from the group consisting of isoparaffins, isoeicosane, isohexadecane and isododecane.

16. An emulsion of claim 15, wherein the oil phase and the water phase of said emulsion both comprise an antioxidant.

17. An emulsion of claim 16, wherein the water phase of said emulsion comprises N-acetyl-L-cysteine.

18. An emulsion of claim 16, wherein said emulsion further comprises a sunscreen.

19. An emulsion of claim 12, wherein said emulsion further comprises a retinoid.

20. An emulsion of claim 12, wherein said silicone gel further comprises a retinoid.

21. An emulsion of claim 9, wherein said composition comprises about 50% to about 70%, by weight, of water.

22. An emulsion of claim 15, wherein said composition comprises about 50% to about 70%, by weight, of water.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 00/13810

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 A61K7/48 C08L83/04 C08J3/09

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08K C08J A61K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 24011 A (MURAD HOWARD) 20 May 1999 (1999-05-20) examples 7,8	
A	US 5 623 017 A (HILL RANDAL M) 22 April 1997 (1997-04-22)	
A	EP 0 827 983 A (GEN ELECTRIC) 11 March 1998 (1998-03-11)	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

5 October 2000

Date of mailing of the international search report

16/10/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Stienon, P

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/13810

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9924011 A	20-05-1999	AU 1307299 A	31-05-1999
US 5623017 A	22-04-1997	DE 69701003 D	03-02-2000
		DE 69701003 T	03-08-2000
		EP 0789061 A	13-08-1997
		JP 9241513 A	16-09-1997
EP 0827983 A	11-03-1998	US 5760116 A	02-06-1998
		AU 3522597 A	12-03-1998
		BR 9704610 A	27-10-1998
		JP 10168318 A	23-06-1998
		US 6060546 A	09-05-2000